The Analyses of the Corrosion Process of a NI-Ti Shape Memory Alloy in Different Environment

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Abstract

In this paper, we investigate the corrosion process of Ni-Ti alloy obtained by the new continius casting method. As the corrosion rate of the material depends on the environment in which the material is located and the corrosion product that slows down the corrosion process over time, in this paper we analyze changes in the base material and the formed corrosion product. This changes were analysed in three different marine environments and at different time intervals of 6 and 12 months. Investigation on the base Ni-Ti alloy, were conducted on base of analyses of the corrosion depth in nm which was measured using the Focus Ion Beam (FIB) method. The linear model was used to calculate the values of corrosion rate during the time of exposure. On the other hand, the corrosion product of the alloy increased over time, resulting in the formation of a corrosive layer on the alloy surface depending on the environment to which it is exposed. The content of the corrosive product was considered using semi-quantitative energy dispersive X-ray (EDX) analysis, and the percentage of oxygen in the corrosive product that appeared on the alloy in all environmental conditions after 6 and 12 months of exposure. As time is raning, corrosion rate is increasing same as percentage of oxygen in each of considered enviroment. Considering results it can be concluded that the formation of the corrosive layer in the sea has a dominant effect on the deceleration of the corrosion process of Ni-Ti alloy, comparing to the all of three considered enviroment.

Keywords: *marine environment, corrosion, Ni-Ti alloy, corrosion, statistical analyses*

1. Introduction

The development of industry in the 21st century requires the use of as resistant, flexible, usable materials as possible which have one or more advantages in relation to the effects of influences such as temperature, corrosion, humidity, stress, etc. Up to know, in the different industry field's well recognized different type of smart materials as pH sensitive materials, chromogenic materials, self-healing materials, shape memory materials and etc.

Since the shape memory effect was discovered in the in 1932 until the present day, additional effect were discovered as super elastic and pseudo elastic effect, high damping capacity and double shape memory (Ölander, A. 1932, Prasad D.S., Shoba C., Varma K.R., 2015). These key thermo-mechanical properties of shape memory alloy were used on base of different shape memory alloys. In that sense, main advantages can be find in different binary or tertian Ni-Ti, Cu-Al-Ni and Cu-Zn-Al, as well as Fe-based alloys (Alaneme K.K. and Okotete E.A 2016). Between this alloys combination Ni-Ti were more useful shape memory alloy.

The shape-memory effect alloy on base Ni-Ti, called as nitinol were used since William Buehler and Frederick Wang recognized shape memory effect in 1962 (Kauffman, G. B. and Mayo, I. 1997). Up to now, different Ni-Ti alloys were use due to specific thermo-mechanical characteristic. The cost of Ni-Ti is high while the most important advantages of Ni-Ti alloys compering to another shape memory alloy were in the highest recoverable strain up to 8 %, application at temperatures from -100^{0}C to 100^{0}C and hysteresis up to 30^{0}C (San Juan, J. 2006). Different production technique and different shape of alloys as disk, wire, road, and spring can be find in different industrial applications.

Last century shape memory materials have find wide range of applications in different industry fields as it is medicine, aircraft, automotive, rail transportation, robotic, fashion and ect. (Mohd Jani, J. et al. 2014) (Huang W. 1998). Unlike other industries such as aviation, the automotive industry and medicine, in recent decade's research has been conducted with the aim of applying SMA in the maritime industry. It has been used so far in different type of ships, under water vehicles (manned and unmanned), and various marine structures as they are offshore applications or wind farm, change of bulb shape, pipe tightening, coupling, subsea devices, elements of thermostat, driven power plant, shell structure, can be find (Ivošević, Š. and Rudolf, R. 2018) (Huang W. 1998).

The complexity of the sea and the atmosphere certainly contributes to the accelerated aging and degradation of the material, and review of influenced parameter are important to understood corrosion mechanism (Ivošević Š. Kovač N., Vastag G. 2021). This degradation can cause partial or total damage of the structural elements of equipment or machine systems. Furthermore, corrosion can be manifest through various forms such as surface, pitting, intergranular, fretting and others forms due to different environment or operation condition where they are exposed. Therefore, it is very important to know the effects of the environment, in order to predict the mechanism of corrosion and the possibility of applying new materials in specific industrial applications.

Conducting experimental research on different shape memory materials in marine environment, the authors of this article previously analyzed the corrosion depth and rate depending of time of exposure and depending of exposed costal and sea water environment (Ivošević Š. Kovač N., Vastag G. 2021), (Kovač, N. Ivošević, Š.; Gagić, R. 2021), (Kovač, N. et al. 2021), (Ivošević Š. et al. 2020). This research, however, compares the depth and rate of corrosion of the Ni-Ti alloy samples depending on the oxygen content in the corrosion product that was formed on alloy surface after the 6 and 12 months of exposure in three different environment.

This article well organize on way that in paragraph 2 were presented material, available data base and methods. Results were presented in paragraph 3 and conclusion in paragraph 4.

2. Materials and Methods

2.1 Materials

In this research shape memory alloy on base Ni-Ti was produced by a combination of vacuum remelting and the continuous casting method. Pure metals of Ni (99.99 wt.%) and Ti (99.99 wt.%) were used to produce NiTi alloys. Totally a sixth samples in the shape of a rod and with the length of 50 mm and diameter of 11,9 mm were analyzed. All samples were cut, processed and prepared for testing (Ivošević Š. et al. 2020). In order to analyses chemical composition of alloy before testing, Inductively Coupled Plasma (ICP) analysis and X-Ray Fluorescence (XRF) analysis were used. On based of mentioned analyses the percentage of nickel (Ni) was between 62,5–62,6% (XRF) and 62,6% (ICP) while the percentage of titanium (Ti) was between 35,9% (ICP and XRF) and 1.4% of Fe (Ivošević Š. et al. 2020).

2.2 Methods

Totally six alloy samples, without previously applied protective coating , after production and preparing for testing were located in three different sea water environment zones (atmosphere, splash and sea water). After the time of exposure, three alloy samples and corresponding corrosion product formed on alloy surfaces were analyzed after 6 months and after 12 months of exposure on each test samples.

In that sense, research were conducted in two direction. In the previous research it is well known that corrosion depth and rate give best information of corrosion process while chemical changes are formed mainly on base of oxygen process. In that sense, in first were analyses corrosion depth on alloy sample and on second were analyzed percentage of oxygen content in corroded product on alloy surface. Two methods were used to calculate corrosion depth and chemical composition of corrosion product.

The Focus Ion Beam (FIB) method was used for the calculation of corrosion depth expressed in nanometer (nm) and energy dispersive X-Ray spectroscopy (EDX) were used to calculated chemical composition of corrosion product.

In the previous research in this field, the increase of corrosion depth on the surface of alloy and oxygen content in the examined alloy were described by linear models. In that sense, in this paper statistical analyses on base of linear model were used to compare the increase in the corrosion rate in nanometer of the examined Ni-Ti alloy and percentage of formed oxygen content in corrosion product for the three different environment after 6 and 12 months of exposure.

2.3 Data bases

All of sixth samples exposed to different environmental conditions after 6 and 12 months of exposure were presented in Table 1. From Table 1 it can be see that no any corrosion or fouling on samples in the air. On other samples exposed to tide and see water can be see fouling and local corrosion spots. More fouling were visible on sample in sea after 12 month where due to long time of exposure and sea moving were cat had of sample.

Table 1. The rods of the Ni-Ti shape memory alloy after 6 and 12 months of exposure to different types of the environment

Time/ months	ATMOSPHERE	TIDE	SEA WATER
6			
12			

The first database were formed on base direction of FIB analyses corrosion depth expressed in nm and include 6 samples of the Ni-Ti alloys. Similarly, 6 samples of corrosion product formed on alloy samples from Figure 1 were also taken into consideration by EDX analyses, and 3 samples were analyzed after 6 months of exposure and 3 samples after 12 months of exposure.

The Ni-Ti samples from Table 1, exposed to three different environment and after 6 and 12 months of exposure were subjected to the FIB analysis with the aim of determining the depth of corrosion. Using well-known linear corrosion model, in this article, available data base of the corrosion depth expressed in nanometers and presented in Table 2. was use for the calculation of corresponding corrosion rate.

Table 2. The corresponding number of empirical data and the average depth of corrosion for the three types of the environment after 6 and 12 months

ATMOSPHERE	6	12	TIDE	6	12	SEAWATER	6	12
No. of points	22	24	No. of points	24	22	No. of points	24	22
Avg. corrosion depth in nm	35.8	64.79	Avg. corrosion depth in nm	37.5	177.92	Avg. corrosion depth in nm	144.27	239.28

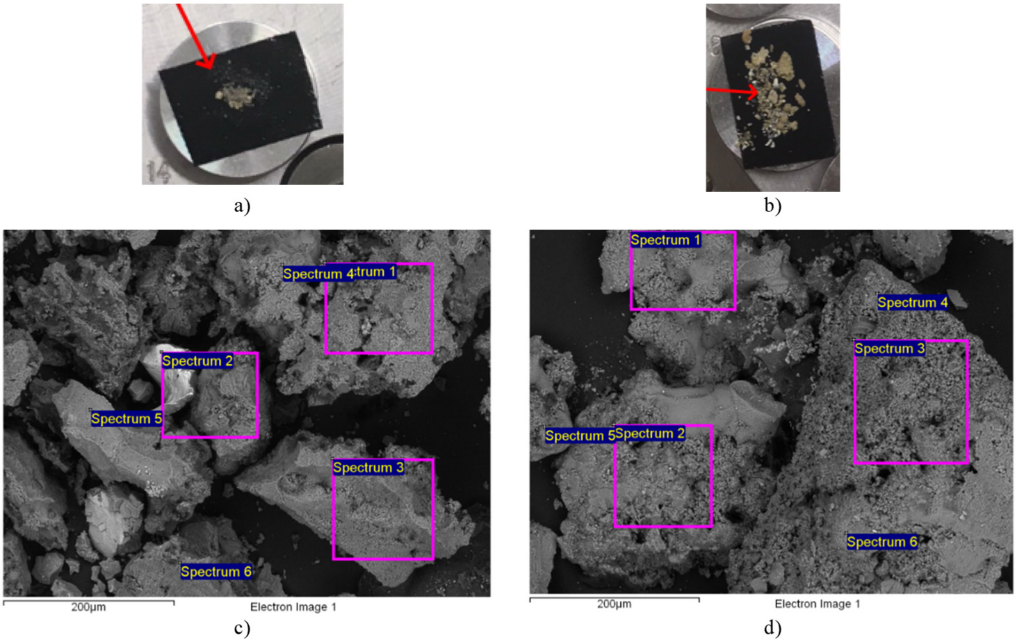

Figure 1. The samples of the corrosion product that was formed in the seawater for 6 months of exposure (a) and 12 months of exposure (b), the corresponding EDX view of the sample after 6 months (c) and 12 months of exposure (d)

On the other way, corrosion product were formed on each of test samples presented on Table 1. Corrosion rust product after 6 months in seawater (Figure 1.a) and 12 months in seawater (Figure 1.b) show that corrosion product increase due to time of exposure. As it was mentioned earlier, based on the corrosion product formed on the alloy surface, the EDX analysis was used to determine the chemical composition of the Ni-Ti samples. On Figures 1.c and 1.d it can be see the tested samples of the corrosion product on the Ni-Ti sample that was in the sea for 6 and 12 months. On Table 3 were presented chemical composition of all Spectrums from Sample from figure 1.d. On same way all samples were analyzed by EDX analyses and corresponding data base of oxygen content for all of three environment were presented in Table 4.

Table 3. The chemical composition of Ni-Ti sample which were presented on Figure 2.b after 12 months in the seawater

Spectrum	C	O	Na	Mg	Al	Si	S	Cl	Ca	Ti	Total
Spectrum 1	12.99	49.74	0.44	0.56	0.19	0.40	0.25	0.68	34.67	0.08	100.00
Spectrum 2	21.84	50.13	0.54	1.44	1.57	2.23	0.76	0.82	18.39	2.27	100.00
Spectrum 3	14.89	52.74	0.69	1.52	1.44	4.83	0.45	0.62	22.49	0.32	100.00
Spectrum 4	14.31	58.84	0.48	0.31	0.18	0.14	0.15	0.05	25.19	0.36	100.00
Spectrum 5	17.38	57.24	1.48	1.12	0.32	0.30	4.02	0.45	15.38	2.31	100.00
Spectrum 6	25.09	56.23	0.62	0.23	0.48	0.30	0.26	0.58	16.00	0.21	100.00
Mean	17.75	54.15	0.71	0.86	0.70	1.37	0.98	0.53	22.02	0.93	100.00
Std. deviation	4.76	3.83	0.39	0.57	0.64	1.87	1.50	0.27	7.27	1.06	
Max.	25.09	58.84	1.48	1.52	1.57	4.83	4.02	0.82	34.67	2.31	
Min.	12.99	49.74	0.44	0.23	0.18	0.14	0.15	0.05	15.38	0.08	

As can be seen from Figure 1.b, and Table 3, EDX analyses were used to get chemical composition of every corrosion product of Ni-Ti alloy samples in all of three considered environment and time of exposure. Number of considered points in data base on base of corrosion product and average of oxygen percentage in each environment after 6 and 12 months of exposure were presented in Table 4.

Table 4. The corresponding number of empirical data and the average values of oxygen content in corrosion products from three types of the environment and exposure periods

AIR	6	12	TIDE	6	12	SEA	6	12
No. of points	12	12	No. of points	13	12	No. of points	18	12
Avg. in % O_2 in corrosion product	14.91	15.03	Avg. in % O_2 in corrosion product	52.97	32.71	Avg. in % O_2 in corrosion product	42.93	51.16

Considering the formed data base from Table 2 and Table 4, it can be concluded that the lowest values of corrosion depth and percentage of oxygen are on the atmosphere.

3. Results and Discussions

3.1 The Analysis of Corrosion Rate and Depth in Relation to Oxygen Content in Corrosion Product of Ni-Ti alloy samples

Considering data base from paragraph 2.3. and using well known linear corrosion model, in Figures 2 and 3 were presented the analyses of corrosion rate of the Ni-Ti alloy and percentage of oxygen content of corrosion product after the time of exposure. On the Figure 2 can be see the dependence of corrosion rate of sample alloys on the percentage of oxygen content in the formed corrosion product on each Ni-Ti alloy samples and in the all of the environment examined. Furthermore, Figure 3 shows the dependence of corrosion depth of Ni-Ti alloys on oxygen content in corrosive product in % (w/w).

Corrosion rate and depth of the examined Ni-Ti alloy samples as well as percentage increase in oxygen in corrosion product formed on alloy surfaces are the lowest in the air and the highest in the seawater. As can be seen from Figure 2 and Figure 3, the rate of change in oxygen in corrosion product is higher in comparison with the examined changes in the alloy in the three types of the environment.

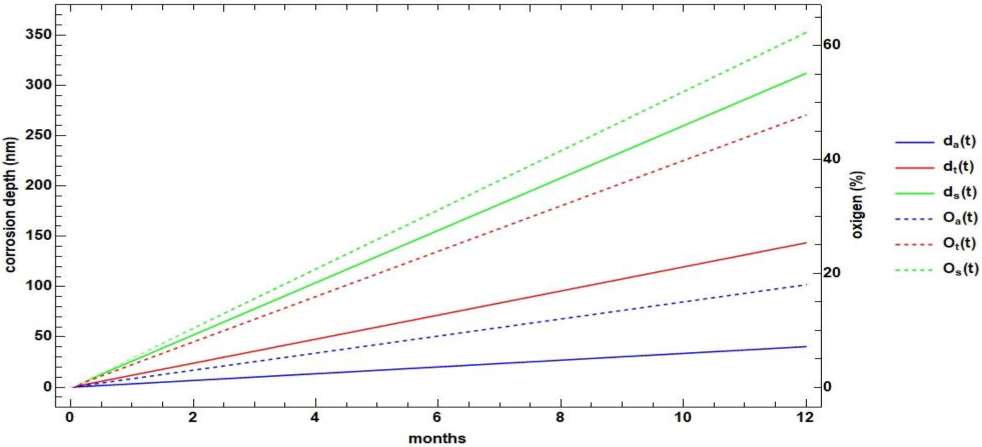

Figure 2. The corrosion rate of the Ni-Ti alloy and oxygen rate in corrosion product in three types of the environment

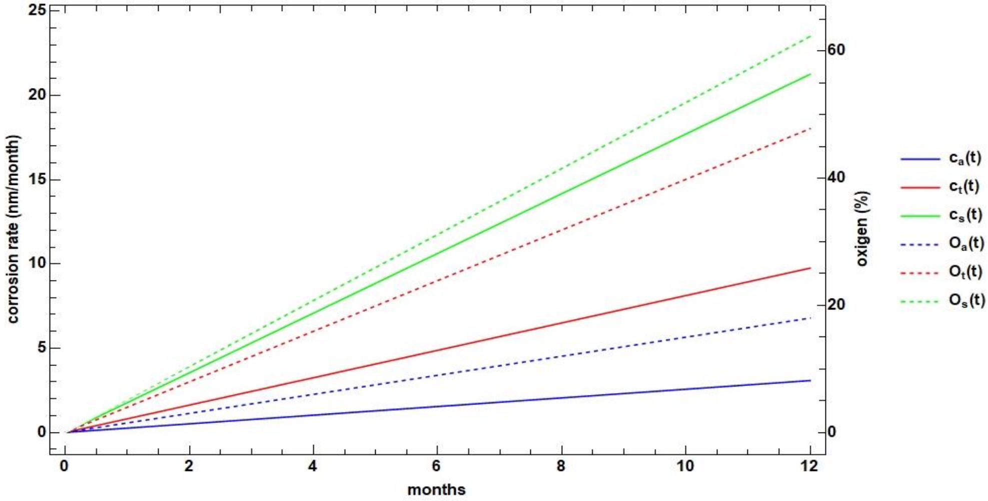

Figure 3. The corrosion depth of the Ni-Ti alloy and oxygen rate in corrosion product in three types of the environment

2.1. The Analysis of Oxygen Content in Corrosion Product

Figure 4 shows the amount of oxygen detected in corrosion product of each test samples in the corrosion product, on the surface of the alloy samples which were exposed to different types of the sea water environment for 6 and 12 months, using the EDX analysis.

Figure 4 shows the amount of oxygen detected by the EDX analysis in corrosion product on the surface of the Ni-Ti alloy samples that were exposed to different types of the coastal environment for 6 and 12 months, respectively.

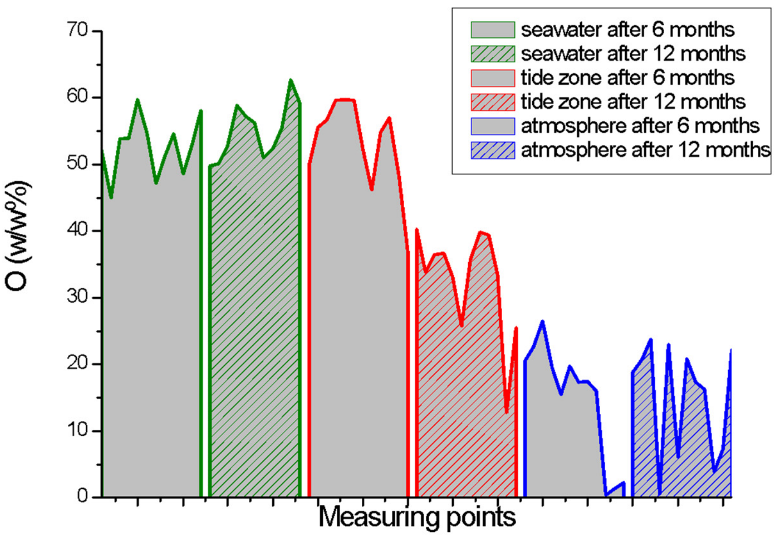

Figure 4. Content of Oxygen in corrosion rust at the tested locations after 6 and 12 months.

Figure 4 shows that the oxygen content detected by the EDX analysis in the corrosion product formed on the Ni-Ti alloy surface varies both, as a function of the type of corrosive environment, and as a function of the length of exposure.

Considering the types of the corrosive environment, Figure 4 shows that in the first 6 months, as expected, the lowest percentage of oxygen was detected in the corrosion product that was formed under the influence of the marine atmosphere. The amount of oxides in the corrosion product formed under the influence of seawater and tides has approximately the same. On the other hand, the values relevant for the seawater influences are significantly higher in comparison with the number of oxides formed under the influence of the air (~40%). Based on the considerations above and on the assumption that the corrosion of alloy elements occurs through the formation of oxides (Kovač, N. et al. 2022), it can be concluded that the degradation of the Ni-Ti alloy is significantly slower under the influence of the air, and approximately the same rate under the action of the other two marine localities.

Several effects were noticed after the analysis of the influence of the length of exposure to different types of the corrosive environment on the amount of the oxygen detected in corrosion product.

- The amount of oxygen on average remains almost unchanged after additional six-month exposure to the influences of the marine atmosphere. There was a more notable increase in scattering between measured points, which indicates that the surface deposits become more heterogeneous over time.
- Seawater with the increase in the length of exposure leads to slightly decreases in the amount of oxides in corrosion product (~ 5%).
- Under the influence of tidal zone, there is, on average a noticeable decrease in the amount of oxygen in the analyzed sample (on average ~ 18%) during the prolonged exposure. This phenomenon can be attributed to the action of waves in tide zones that wash away the formed corrosion products over time from the alloy surface.

Therefore, the formation of corrosive products during prolonged exposure of a Ni-Ti alloy to the corrosive environment undergoes the greatest changes under the influence of tidal zone.

4. Conclusions

In this paper were analyzed the changes caused by corrosion process on Ni-Ti alloy samples and formed corrosion product of alloy surface, that was exposed to different sea water environment after 6 and 12 months of exposure. Corrosion depth and rate of the examined Ni-Ti alloy samples and percentage of formed oxygen content in corrosion product in three different types of environment (sea water, air and tides) were analyzed by means of a linear model of corrosion development. The obtained results confirmed as follow:

- The lowest increase in the depth and rate of corrosion of the examined alloy is in the atmosphere compared,
- The increase in oxygen in corrosion product is higher than the corrosion rate of the examined Ni-Ti alloy samples in all types of the environment,
- highest increase of oxygen percentage was observed in tidal zone, which could be attributed to the dynamic processes of sea waves, and interchangeable of wet and dry cycles.
- The results of the EDX analysis indicated that the oxygen content in the corrosion product that was formed on the surface of the Ni-Ti alloy depends on both, the corrosive environment and the length of exposure of the alloy to such environment.
- The lowest amount of oxides was registered in the corrosion product formed under the influence of the air and such oxide content was the least changed over time.
- The greatest changes in oxygen content as a function of time were detected in the corrosion product formed under the influence of tide.

The future research should investigate other shape memory materials and the impact of dependence of corrosion process comparing the other chemical elements in corrosion product and alloy samples. That elements could be chlorides, carbon, etc. over the extended period of time.

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